An Introduction to "Standard Bundles" in NIST DTSA-II

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Using a complex standard

DTSA-II has added support for “standard bundles”, collections of spectra designed to simplify the process of quantifying unknown spectra using “complex” or “similar standards”

Standards

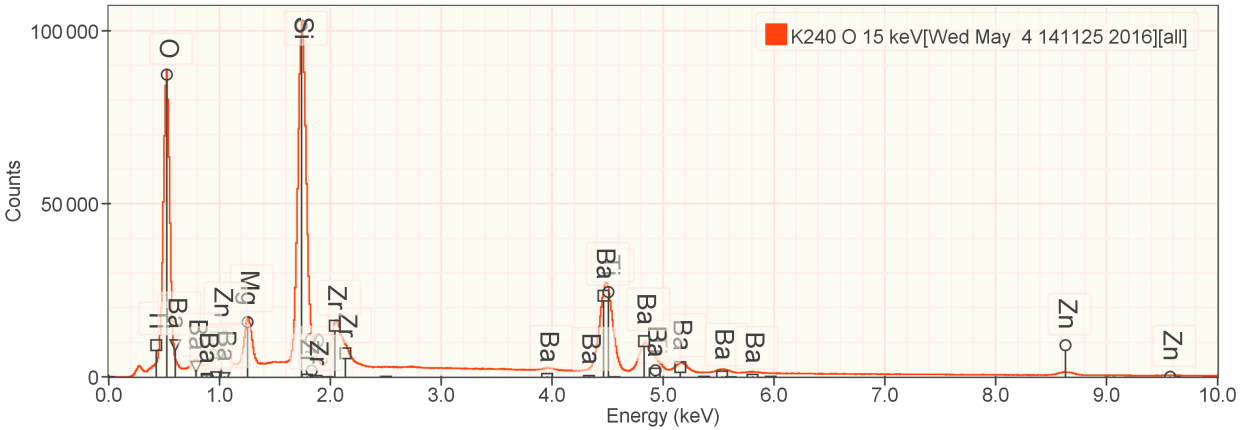
- Spectrum quantification is based on comparing the *unknown spectra* with spectra from materials of *known composition*.
- To a good approximation, the composition in the unknown equals[1] the composition in the standard times the ratio of the intensity[2] in the unknown relative to the standard.

$$C_u \approx C_s \frac{I_u}{I_s}$$

[1] Ignoring “matrix corrections”

[2] Where *intensity* is understood to mean the intensity in a characteristic x-ray peak associated an element.

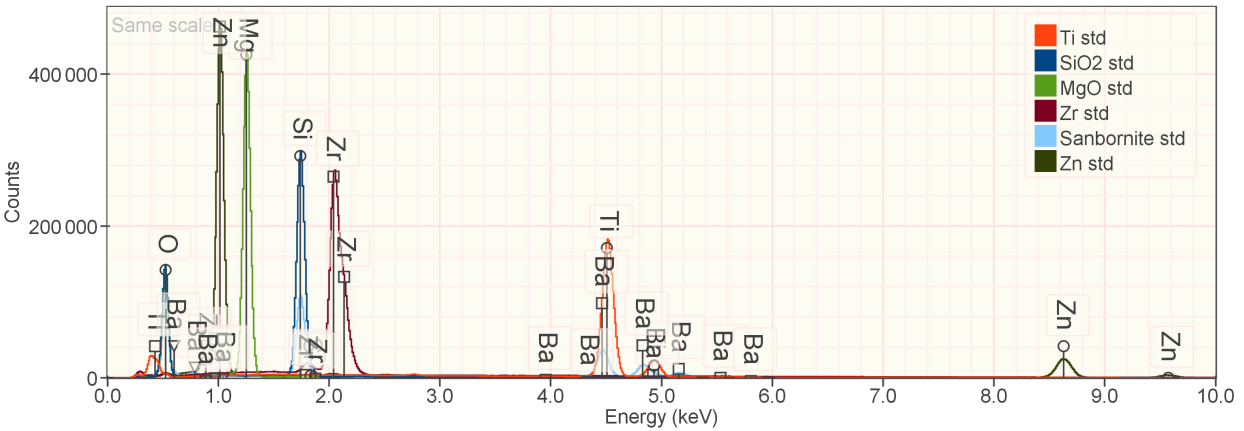
Example – Simple standards



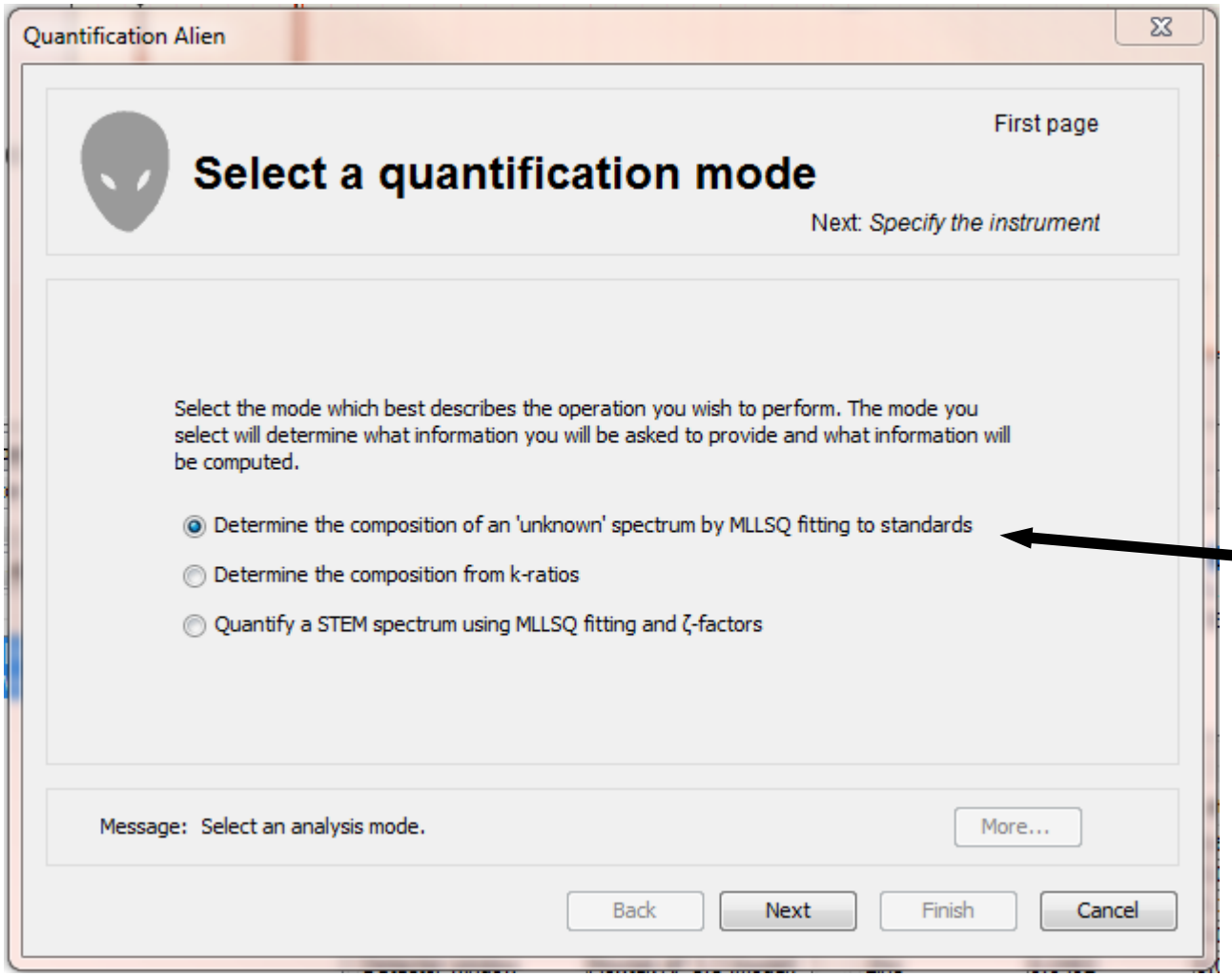
Element	Z	Mass Frac
Oxygen	8	0.34
Magnesium	12	0.0302
Silicon	14	0.187
Titanium	22	0.06
Zinc	30	0.0402
Zirconium	40	0.074
Barium	56	0.2687
Total		1.0001

Standards:

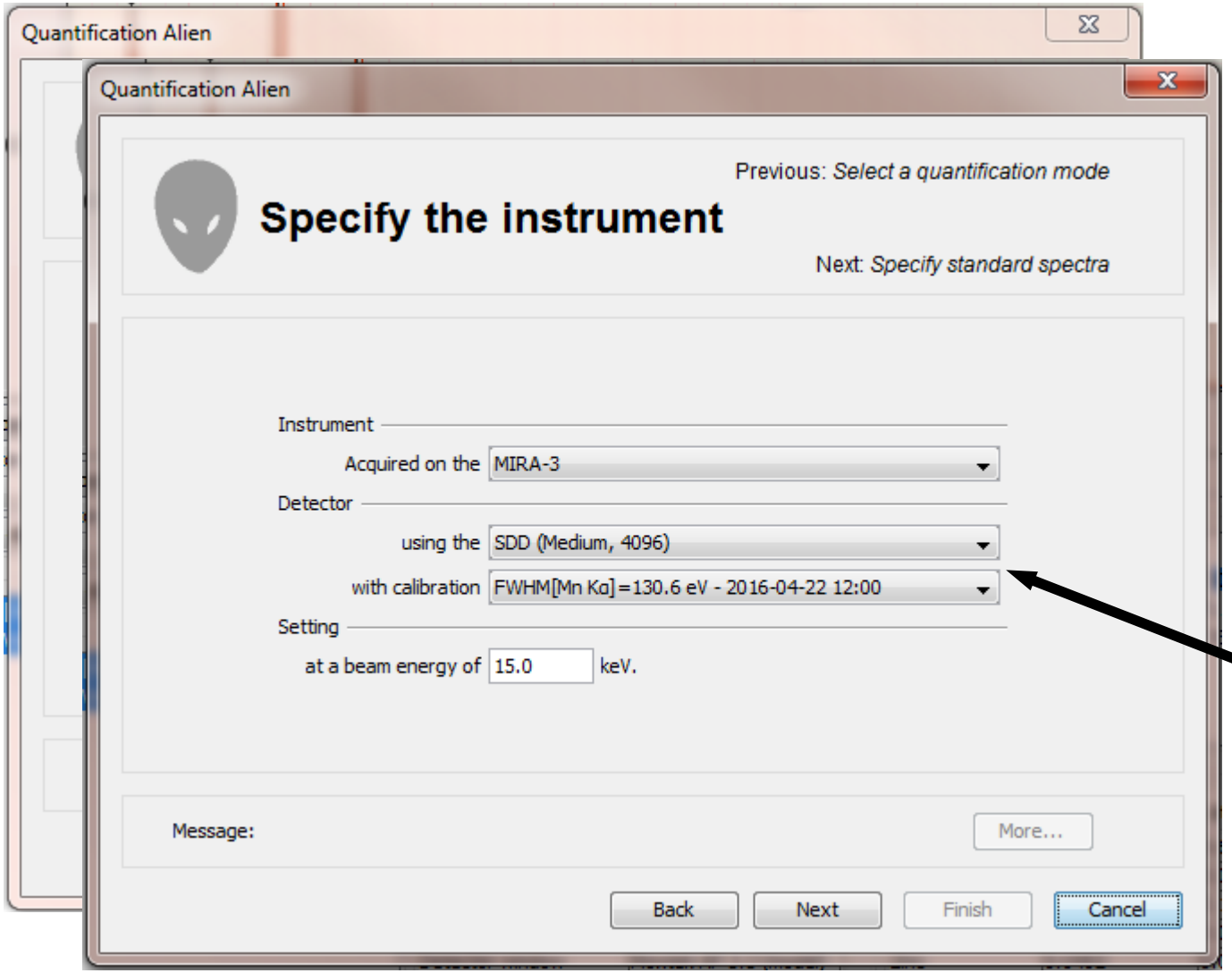
Si	SiO_2
Mg	MgO
Ti	Ti metal
Zn	Zn metal
Zr	Zr metal
Ba	$Ba(Si_2O_5)$
O	calculated



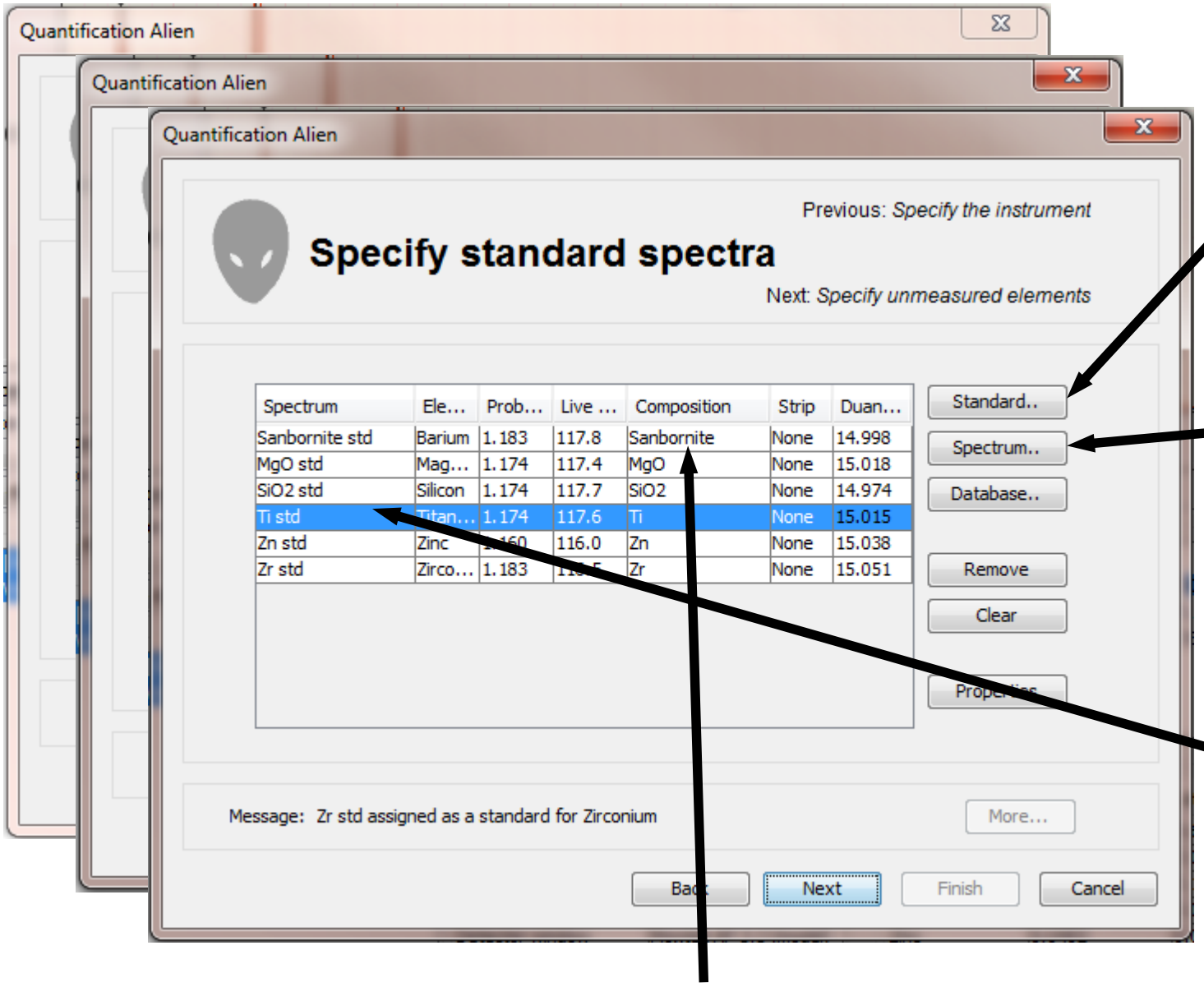
While SiO_2, MgO and $Ba(Si_2O_5)$ contain multiple elements, the elements within each standard do not interfere with each other so the peak shapes are equivalent to the pure element peak shapes.



Select quantify a bulk material using standards fit using multiple linear least squares fitting.



Verify that the default instrument and detector information read from the spectrum/spectra is correct.

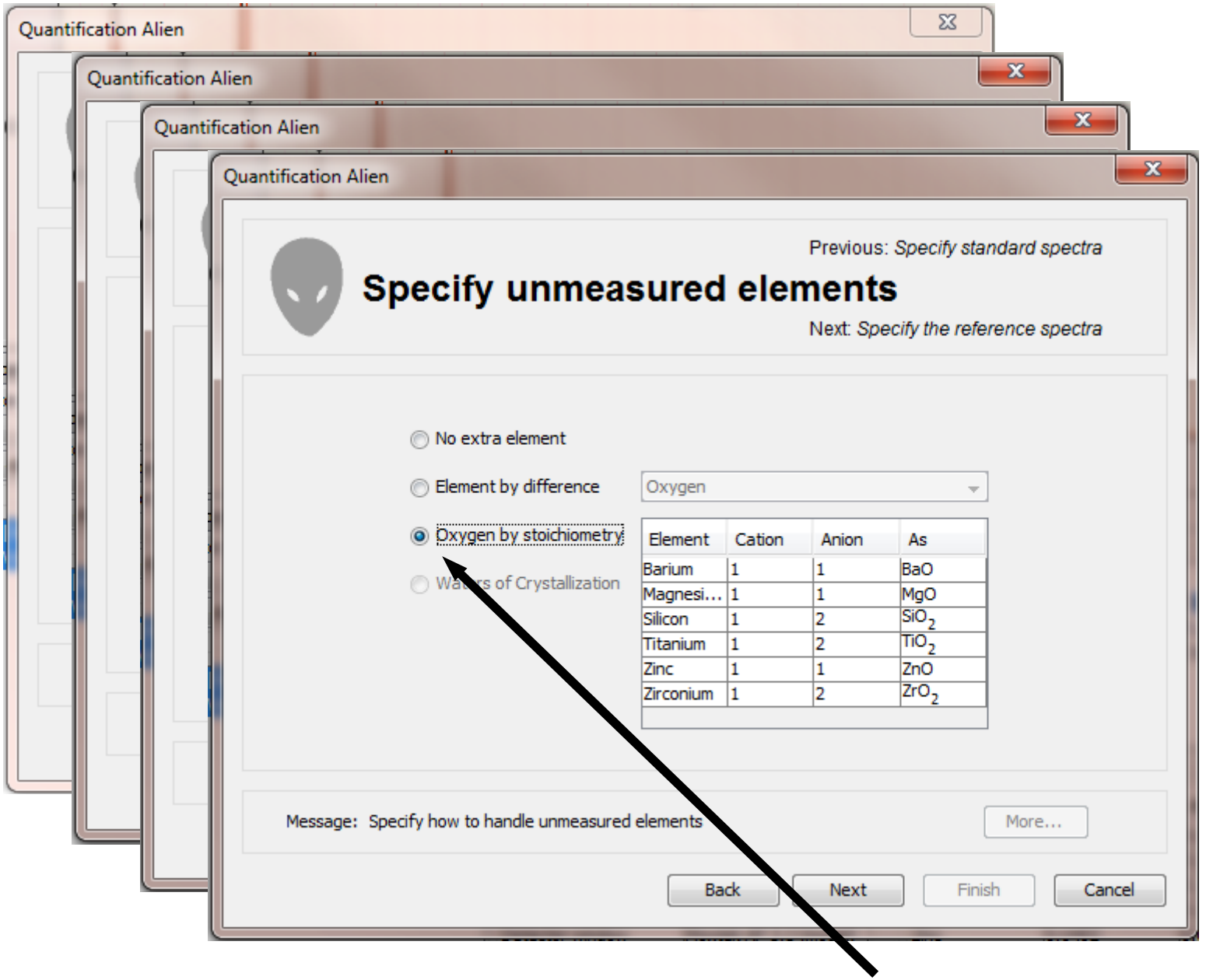


Specify standard bundles using this button.

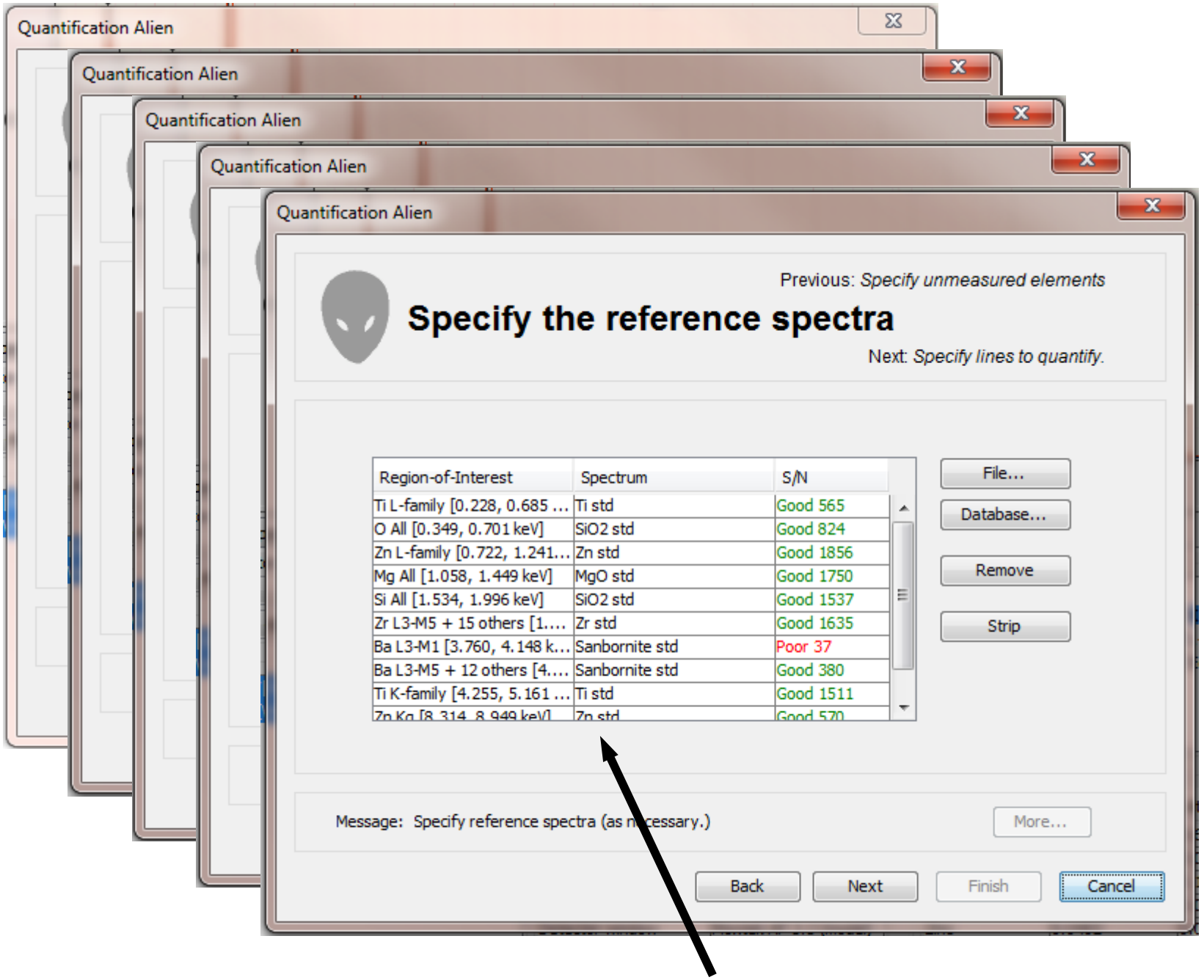
Alternatively, specify raw spectra using this button.

The standards you have specified show up here along with information about the standard.

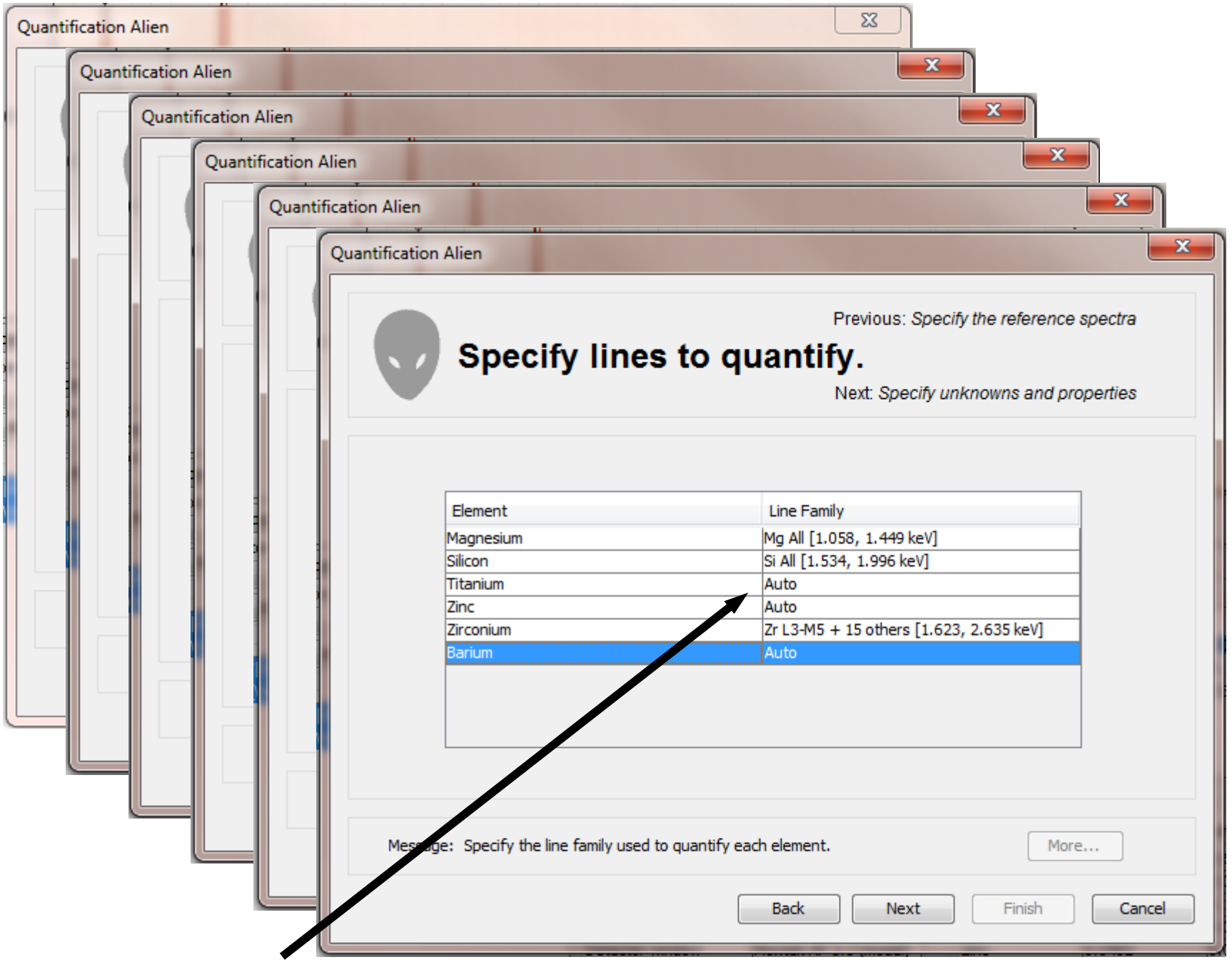
You may be asked to provide compositional information if this information isn't present in the spectrum.



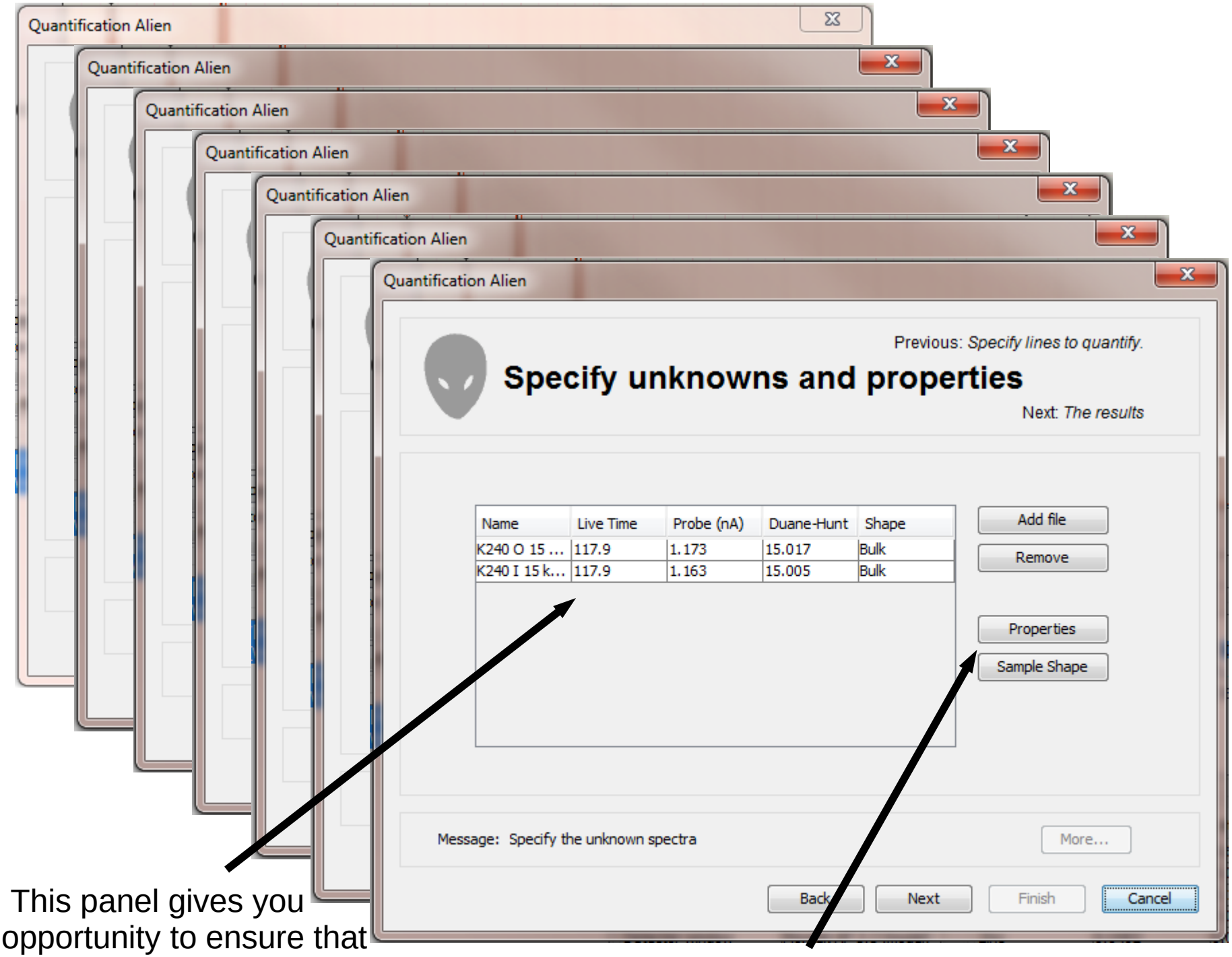
You may either choose to provide a standard for O or you may choose to have the quantity of O computed using an assumed stoichiometry (which you can edit if the default assumptions aren't right.)



Because we chose simple standards, there is no need to specify separate reference spectra. (The standardized elements don't interfere with other elements in the standard.)

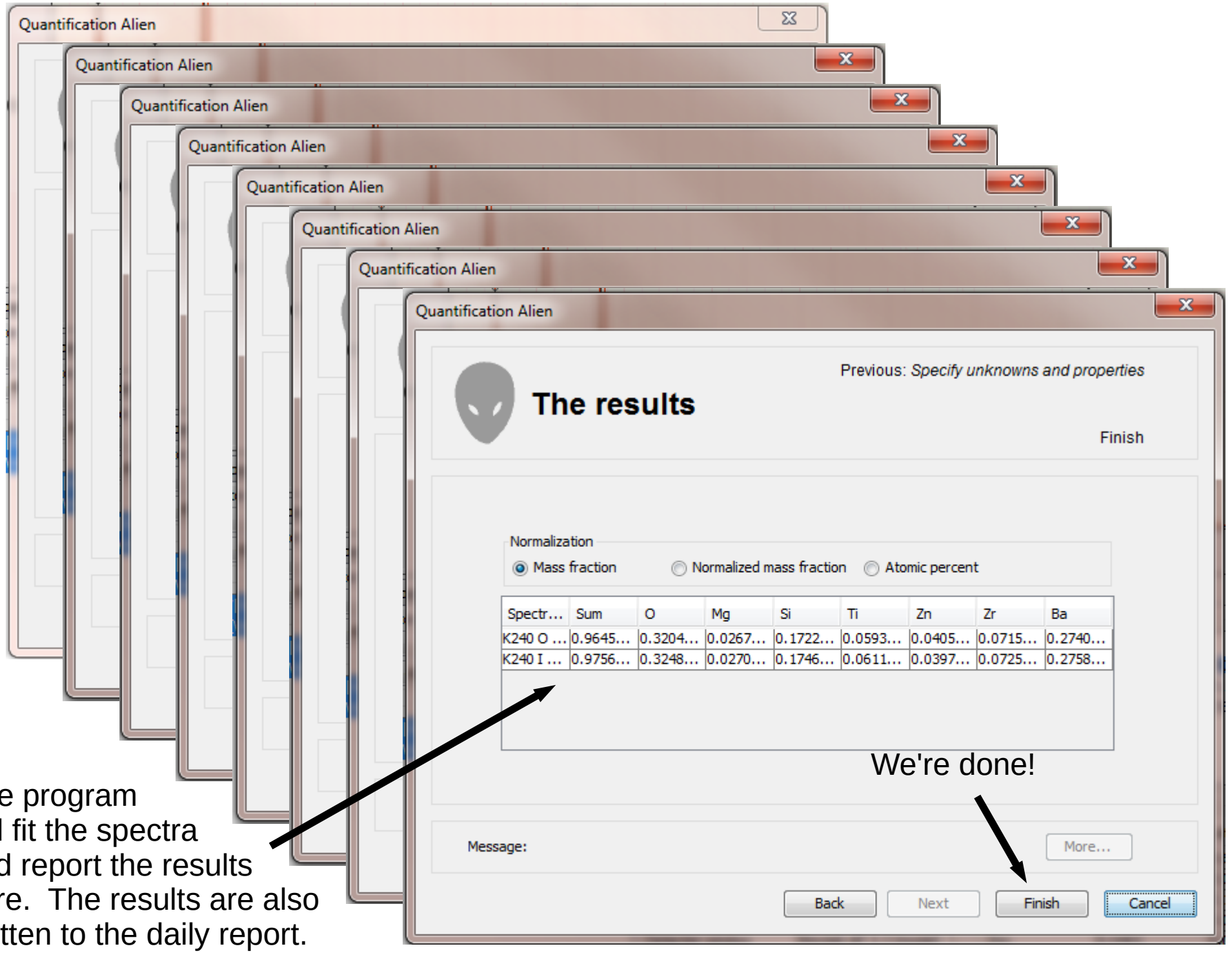


You can allow DTSA-II to select which line to use to quantify, or you can force it to use the line that you specify.

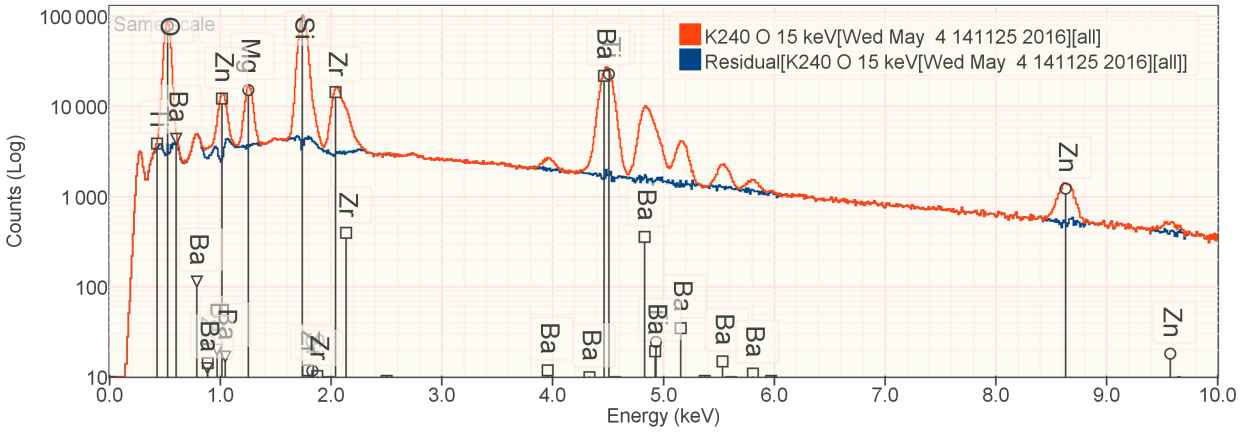


This panel gives you an opportunity to ensure that all the necessary data is available for the unknowns.

Update spectrum properties here.



The program will fit the spectra and report the results here. The results are also written to the daily report.



The original spectrum and the residual. Every element has been accounted for!!

Name	O	Mg	Si	Ti	Zn	Zr	Ba
K240 O	32.0	2.7	17.2	5.9	4.0	7.1	27.4
K240 I	32.5	2.7	17.5	6.1	4.0	7.3	27.6
Average	32.3	2.7	17.3	6.0	4.0	7.2	27.5
Nominal	34.0	3.0	18.7	6.0	4.0	7.4	26.9
Difference	-5%	-11%	-7%	0%	0%	-3%	2%

Ok result, but not great. I could probably have done better replacing the MgO standard with pure Mg and the SiO_2 standard with pure Si. I suspect the source of the error is charging (particularly with the MgO standard.)

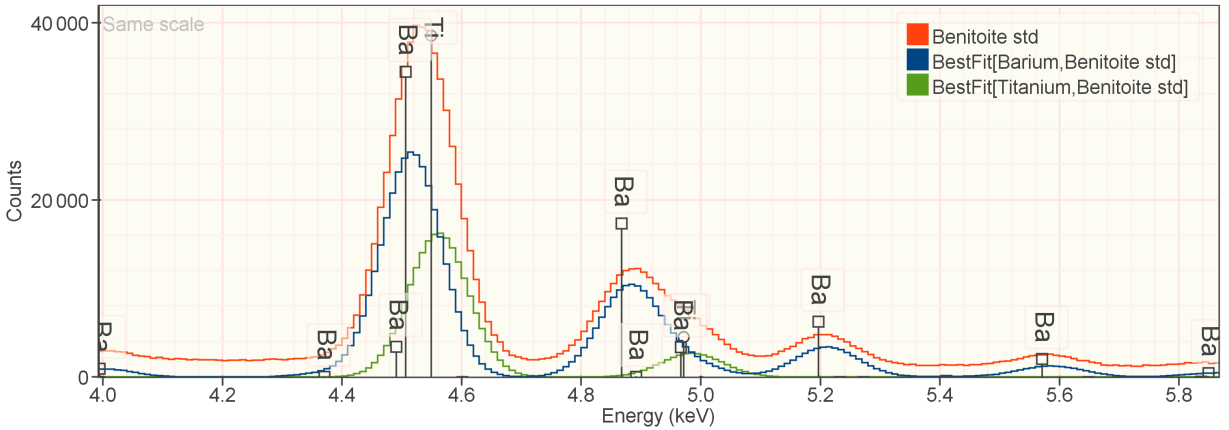
$$C_u \approx C_s \frac{I_u}{I_s}$$

- The validity of this approximation is enhanced when the composition of the unknown and the standard are approximately equal.

- This condition is called a “similar standard”

- Similar standards don't need to contain all the elements in the unknown.
- Similar standards can contain elements not in the unknown.

Example – Similar/Complex Standards



Remotivate:

Selecting a standard with composition similar to our unknown reduces the need for matrix correction and is more likely to produce accurate results.

Like our unknown glass, Benitoite contains Ba and Ti.

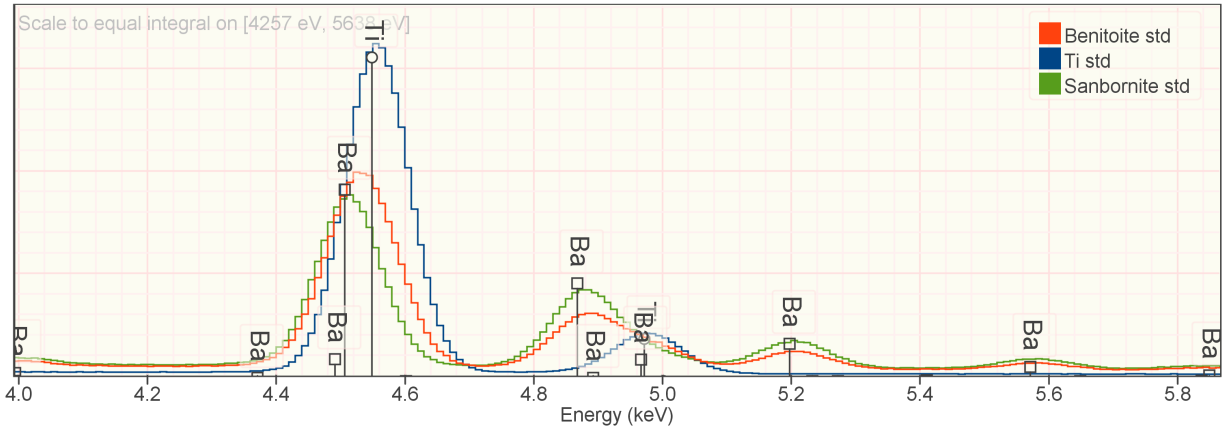
	Benitoite	"Unknown"
Barium	33.22 %	26.9 %
Titanium	11.58 %	6.0 %

Not in exactly the same proportions but similar.

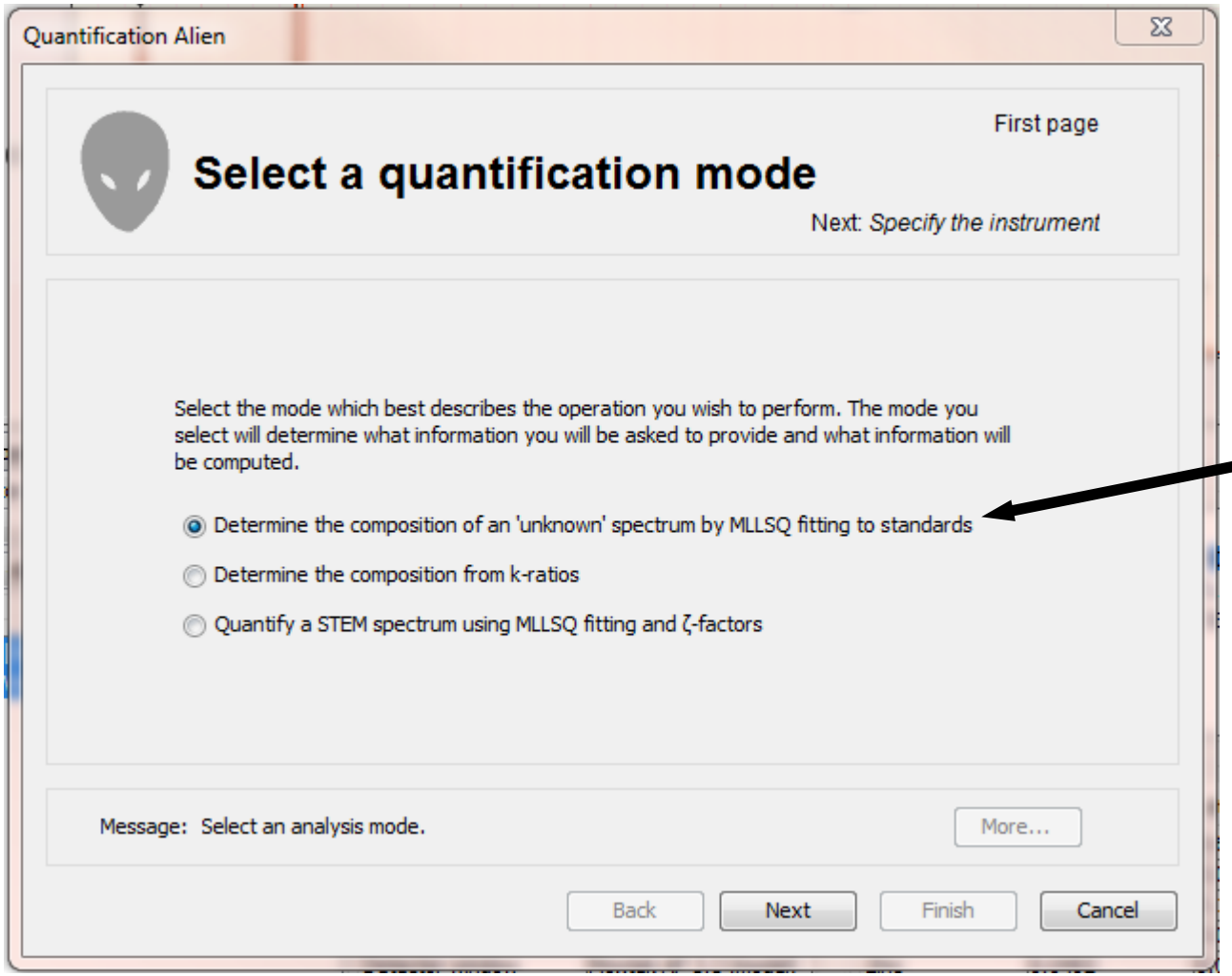
But there is a nasty overlap between Ba and Ti! Can we really use Benitoite as a standard?

References

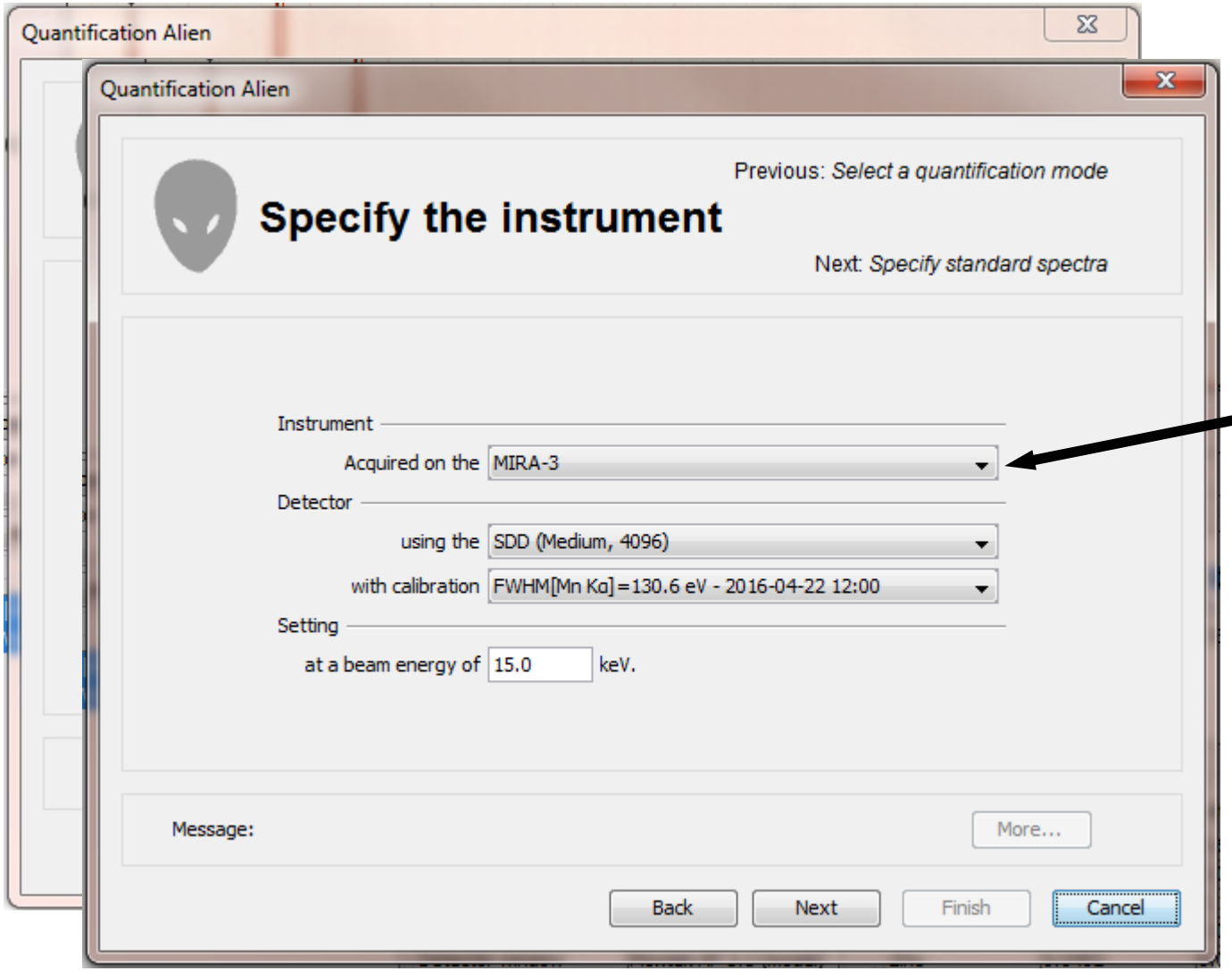
- Can we use Benitoite as a standard?
  - Yes, if we tell the program what pure Ba and pure Ti look like!



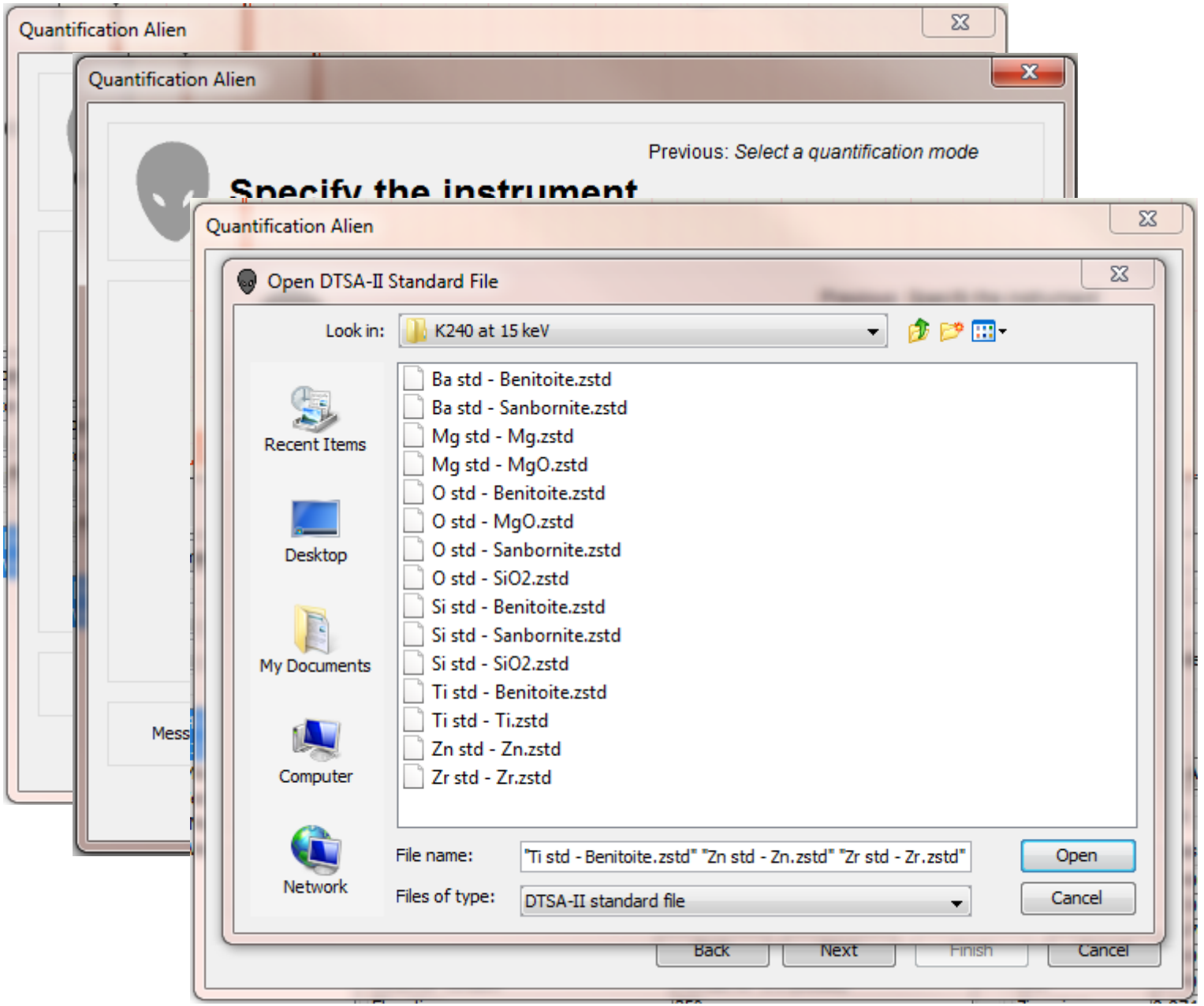
We provide “references” (Ti metal and $Ba(Si_3O_9)$) that tell the program what unobstructed Ti K and unobstructed Ba L lines look like.



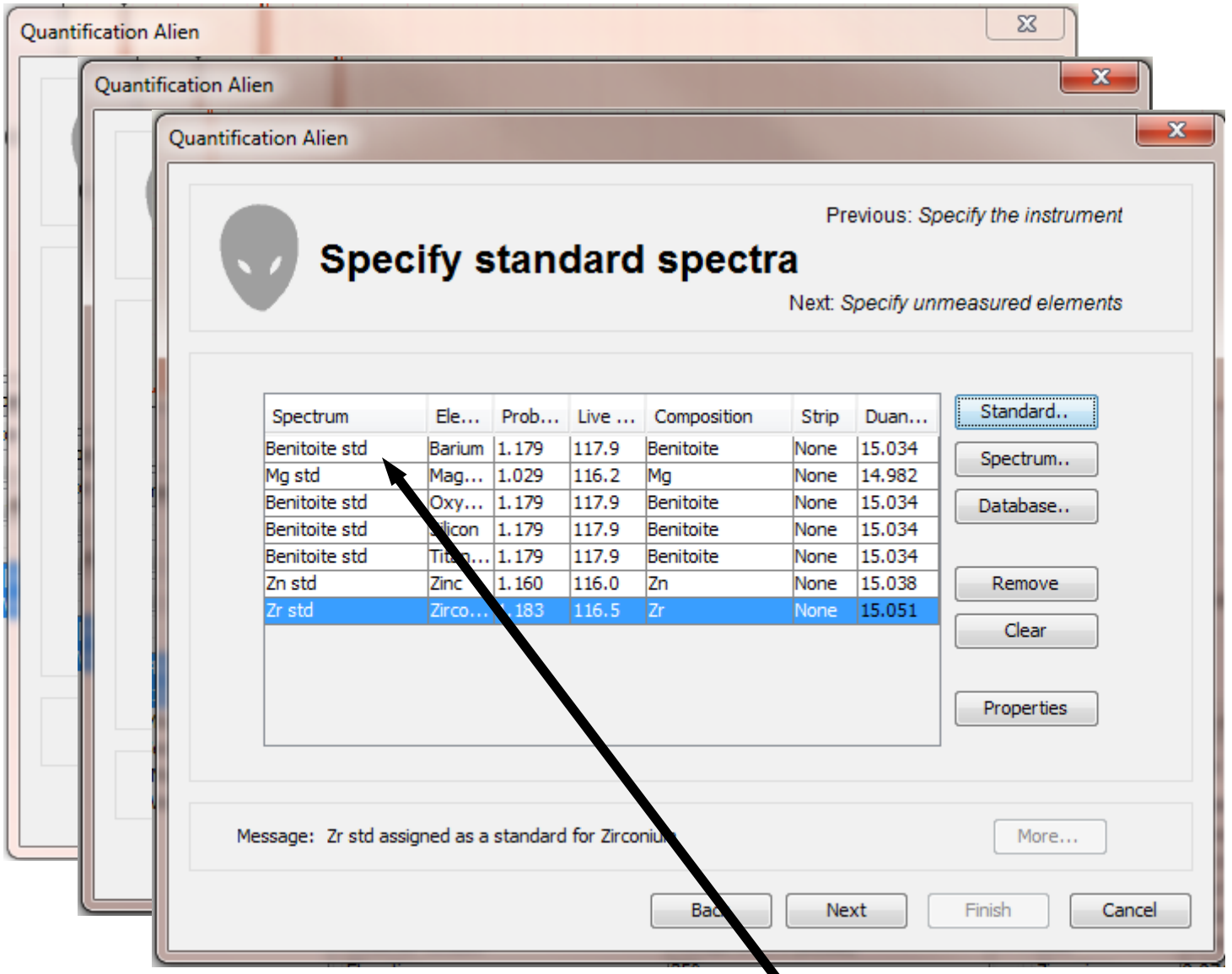
Same as before.



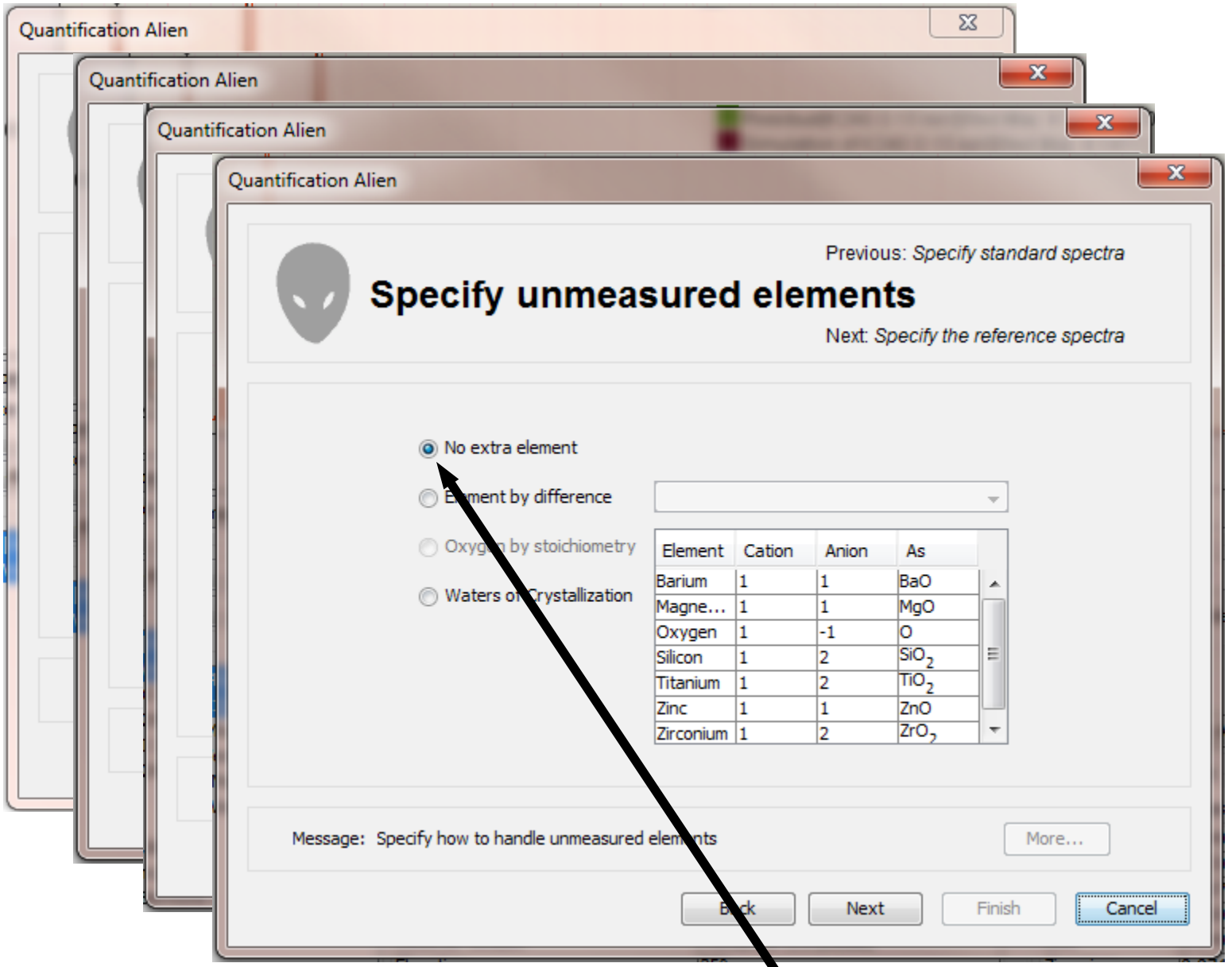
Same as before.



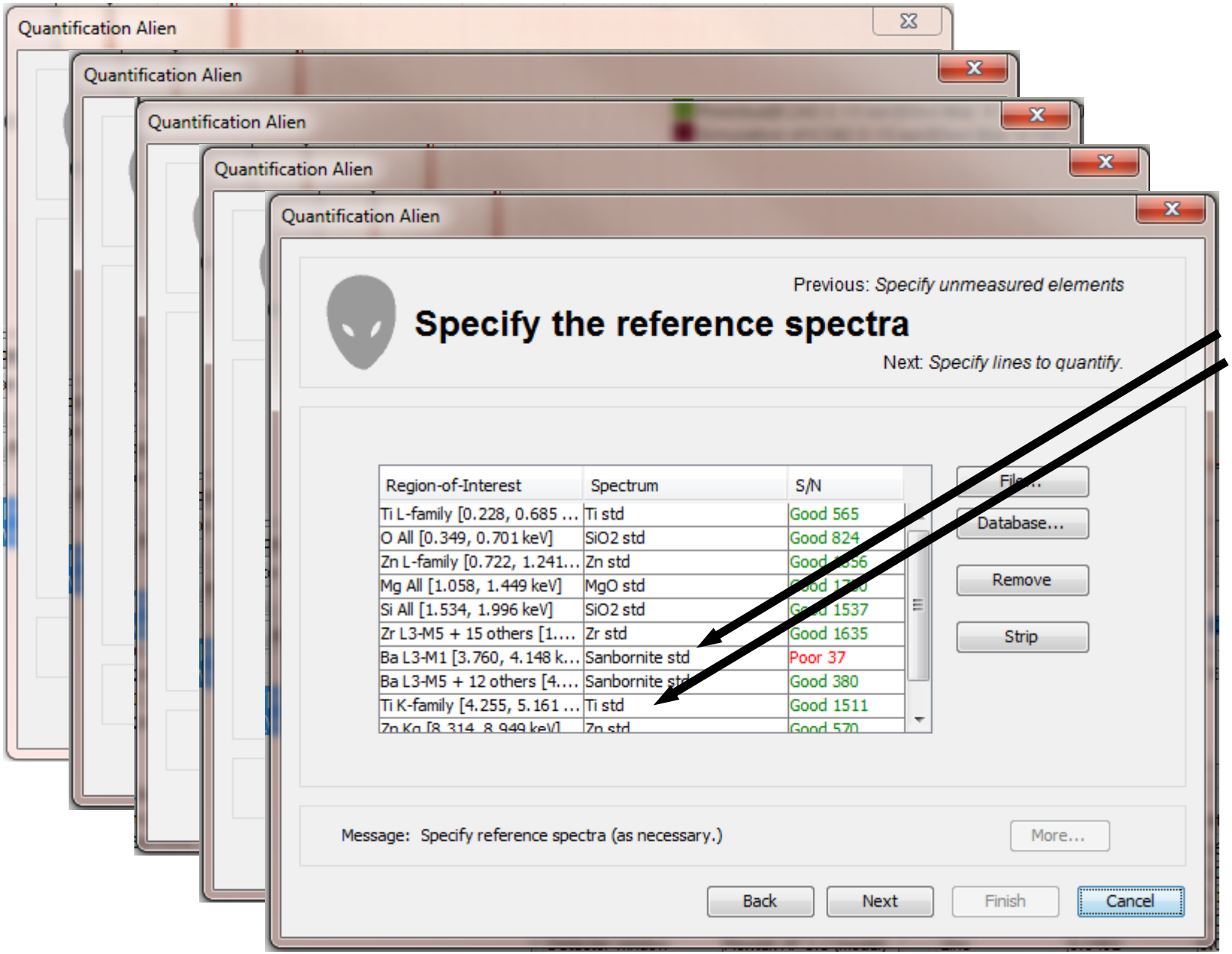
Same as before.



This time we specify Benitoite as a standard for Ba, Ti, Si and O. (Previously we'd compute O.)
Mg is now pure Mg and Zn and Zr are also pure elements.

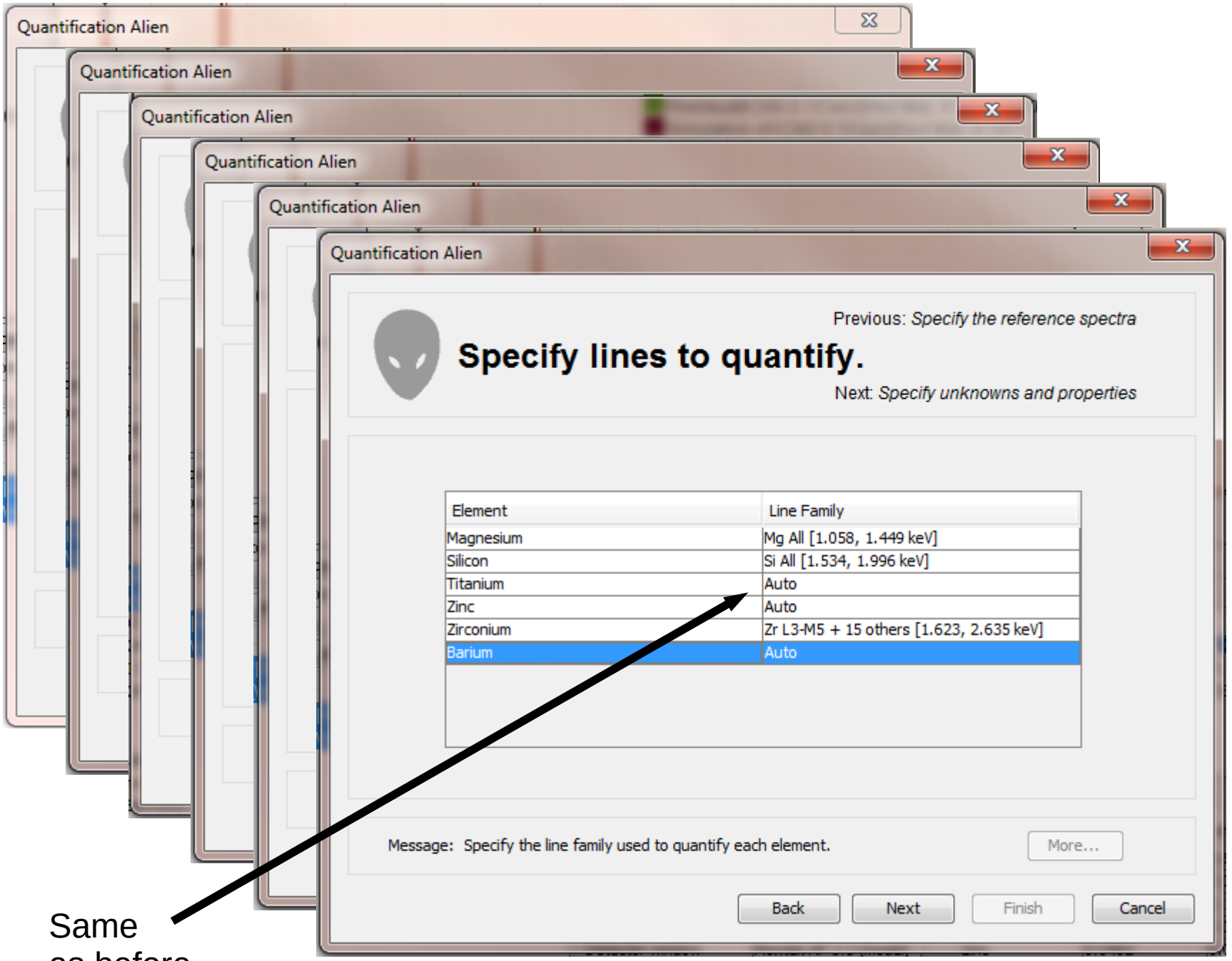


Now we're measuring O because we can measure O accurately with a similar standard.

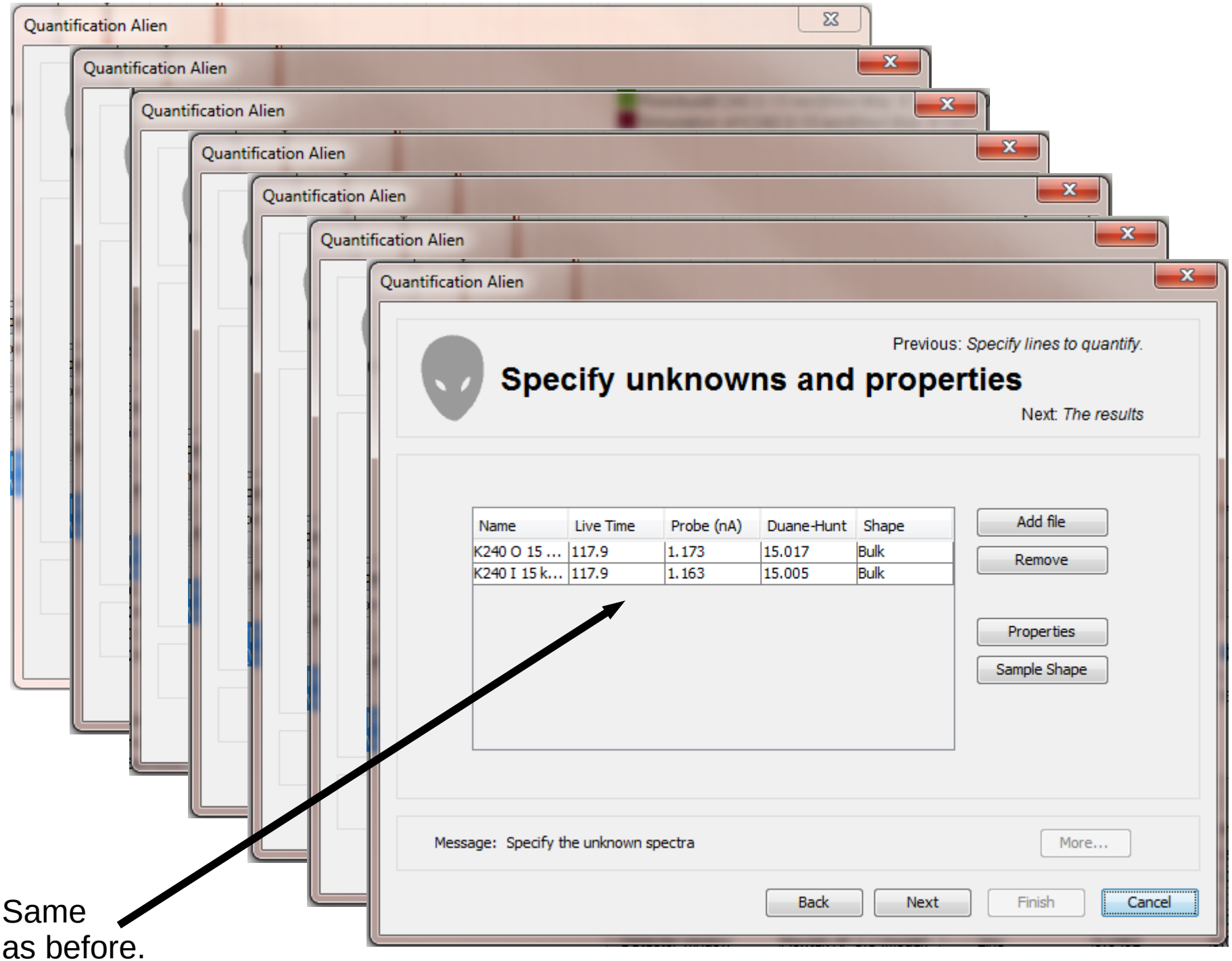


Big difference!!

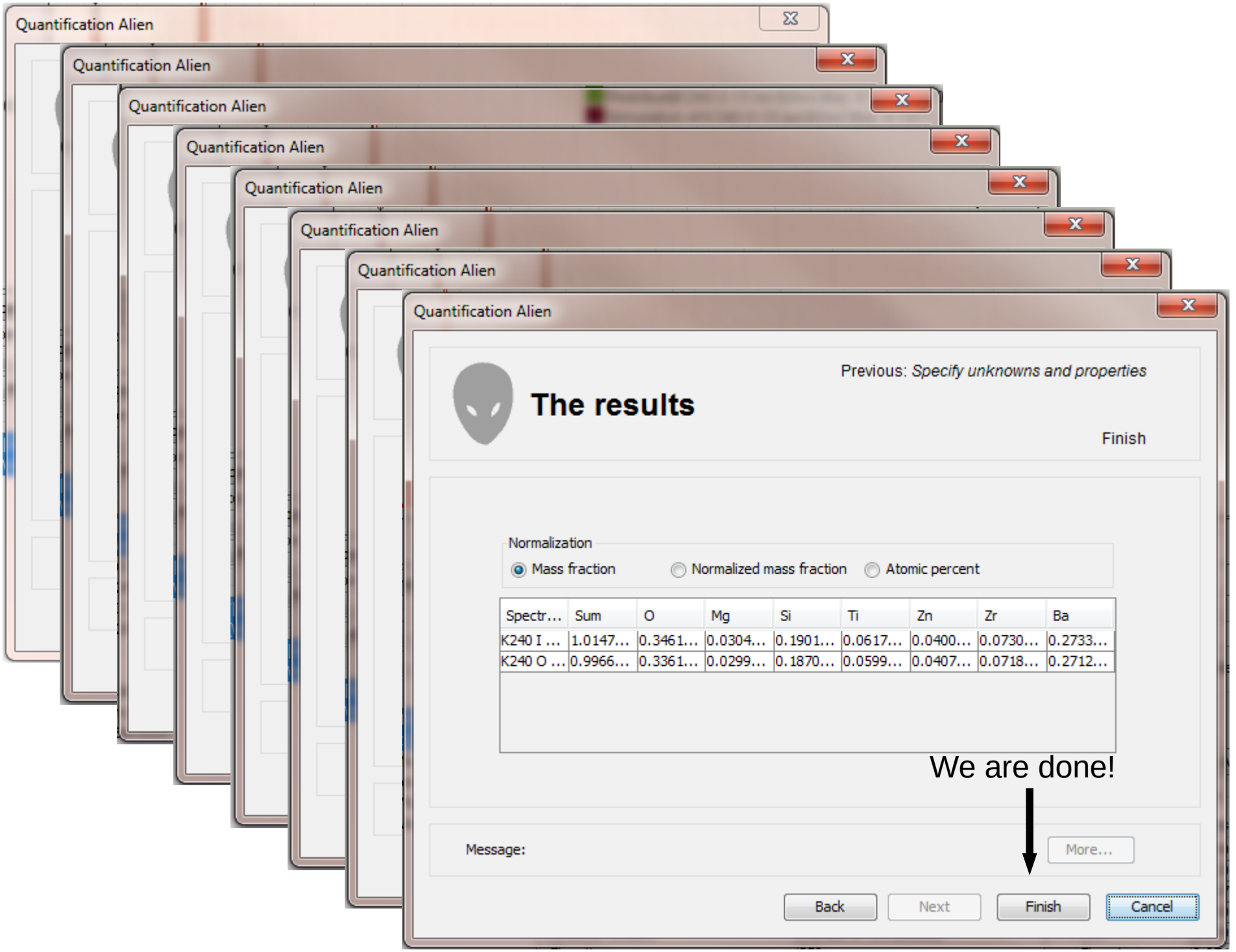
This time we need to specify spectra as “peak shape” references to help us to extract the intensity information from both the standard and the unknown for Ba and Ti.



Same
as before



Same as before.


Quantification Alien
Quantification Alien
Quantification Alien
Quantification Alien
Quantification Alien
Quantification Alien
Quantification Alien
Quantification Alien
Previous: Specify unknowns and properties
The results
Finish
Normalization
Mass fraction
Normalized mass fraction
Atomic percent
Spectr... Sum O Mg Si Ti Zn Zr Ba
K240 I ... 1.0147... 0.3461... 0.0304... 0.1901... 0.0617... 0.0400... 0.0730... 0.2733...
K240 O ... 0.9966... 0.3361... 0.0299... 0.1870... 0.0599... 0.0407... 0.0718... 0.2712...
We are done!
Message:
More...
Back
Next
Finish
Cancel

Results

Simple standards

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Similar standards

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Average	34.1	3.0	18.9	6.1	4.0	7.2	27.2
Nominal	34.0	3.0	18.7	6.0	4.0	7.4	26.9
Difference	0%	0%	1%	1%	0%	-2%	1%

WEE HEE!
WOO HOO!

As is often the case, similar standards produce more accurate results than simple standards.

Making similar standards easy

The problem:

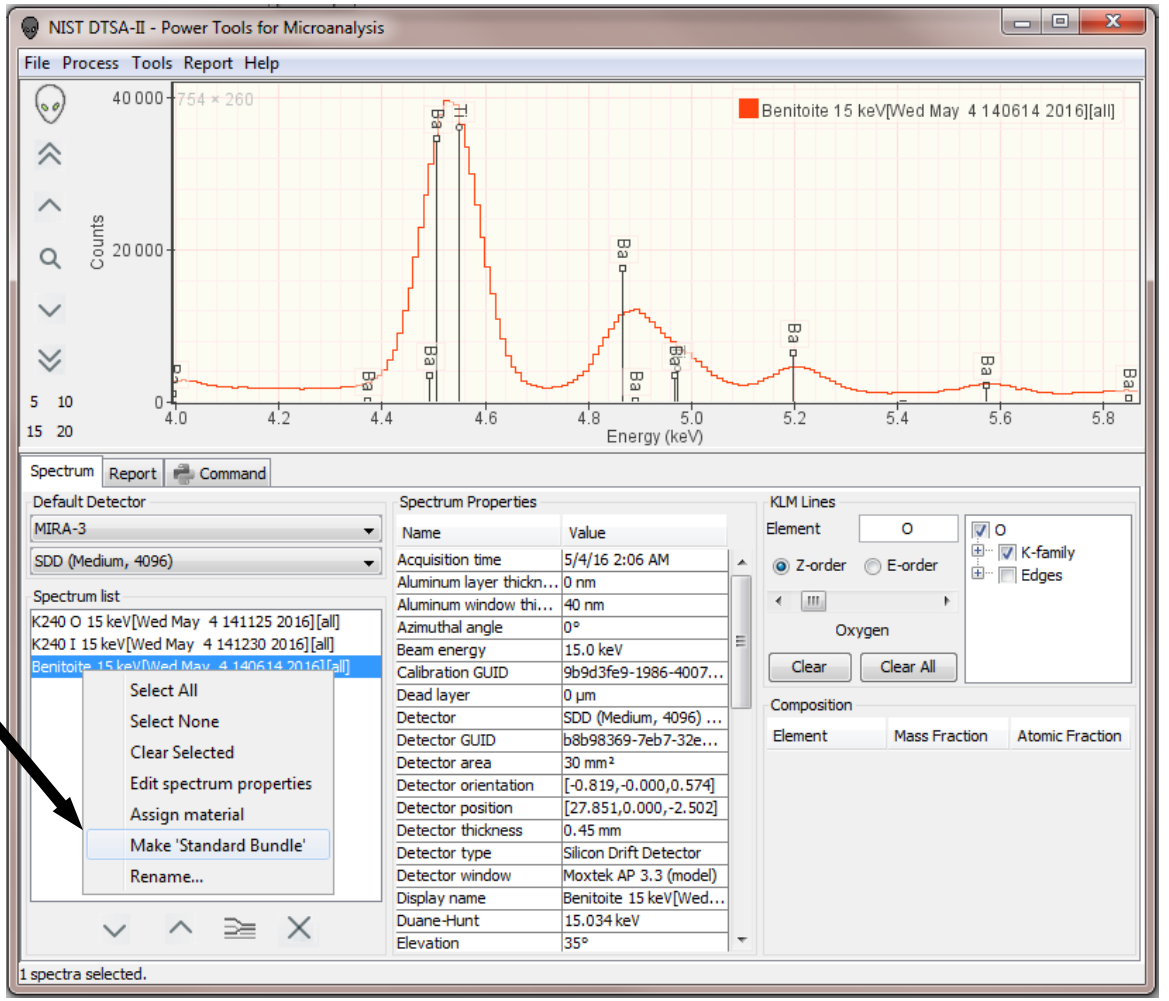
Similar standards often require reference spectra and specifying reference spectra every time is tedious!

The solution:

Bundle standard spectra with the reference spectra required to use them.

One or more spectra

A spectrum bundle can be created from one or more spectra collected under identical conditions from the same material. Highlight the spectra in the spectrum list before selecting “Make 'Standard Bundle'”.



A word about collecting standards

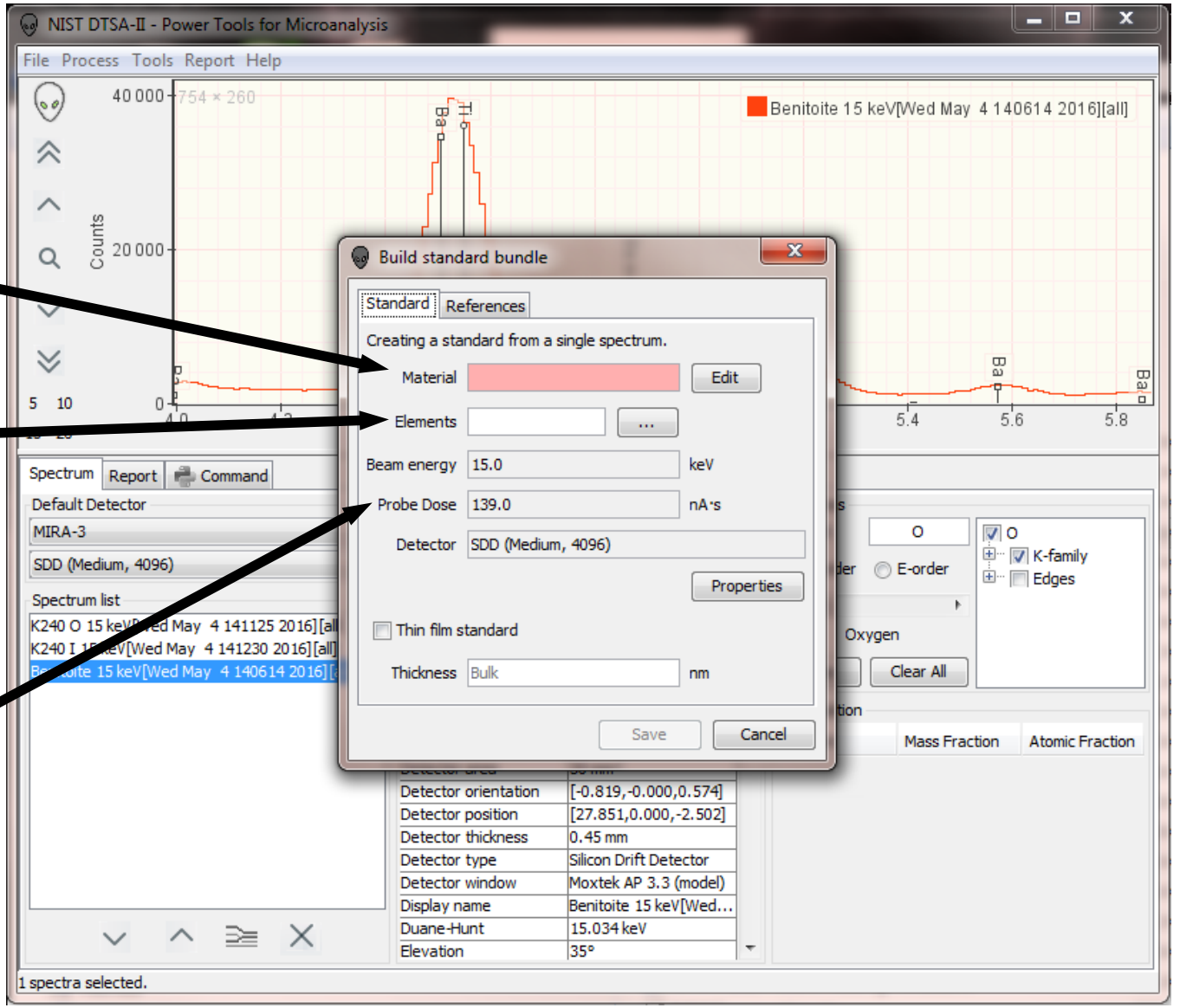
- Standards have to be high quality spectra collected under well controlled conditions from a homogeneous material.
- Many potential pitfalls can be detected by collecting multiple spectra from different points on the same material, comparing the spectra and later combining them into a single spectrum.
- It is better to collect 5 spectra of 60 seconds each, compare and combine them to form one 300 second standard than to collect one 300 second spectrum.
  - If all five spectra are essentially identical, it raises your confidence in the reliability of the spectra (no contamination, geometric effects, pits, ridges, current drift,...)
  - Even if you end up discarding one or two spectra, you feel confident the other three or four are of high quality.

Describing the standard

Specify the composition of the standard.

Specify the elements for which this material can be a standard.

Also verifies that all the necessary instrument data is present.



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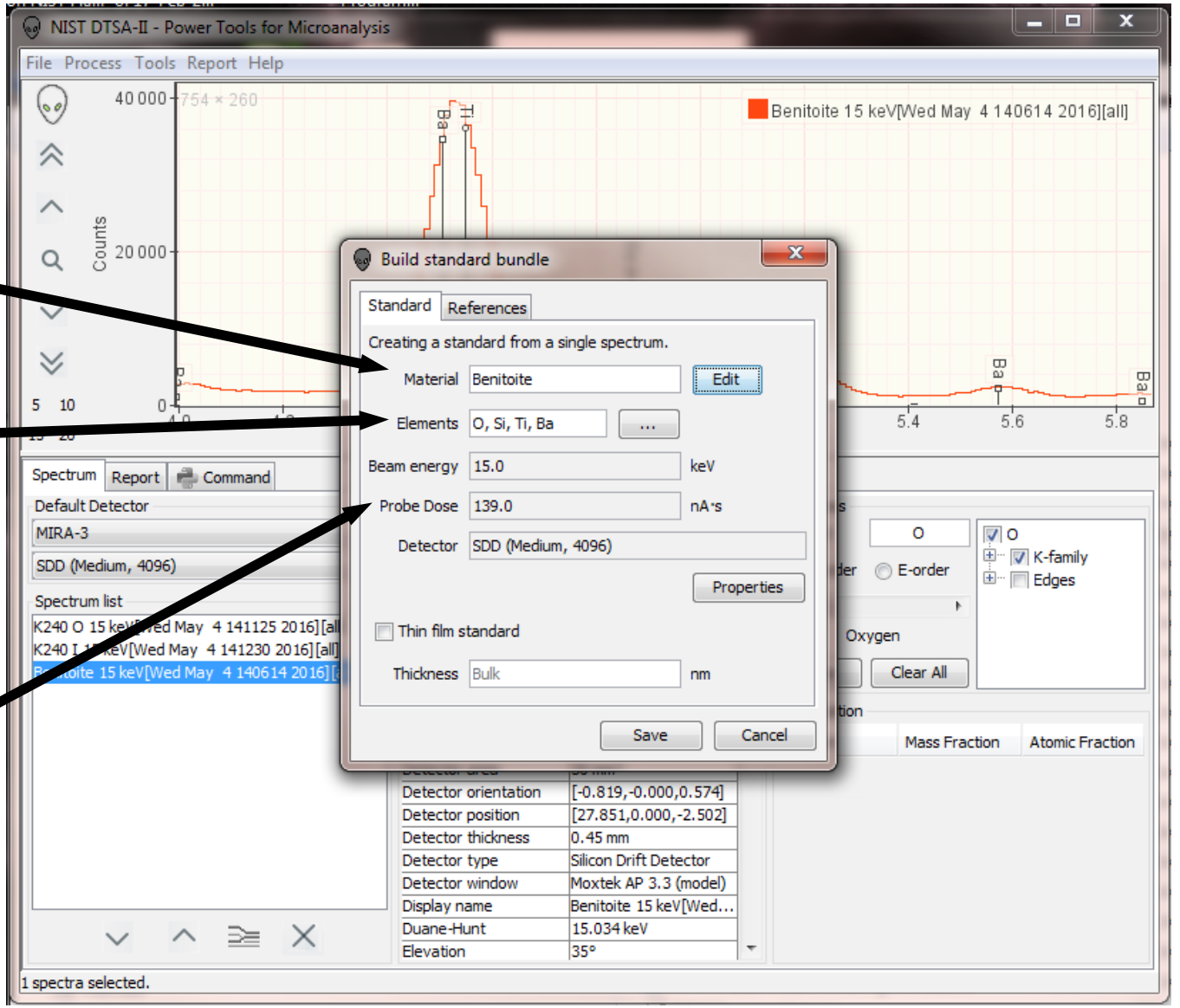
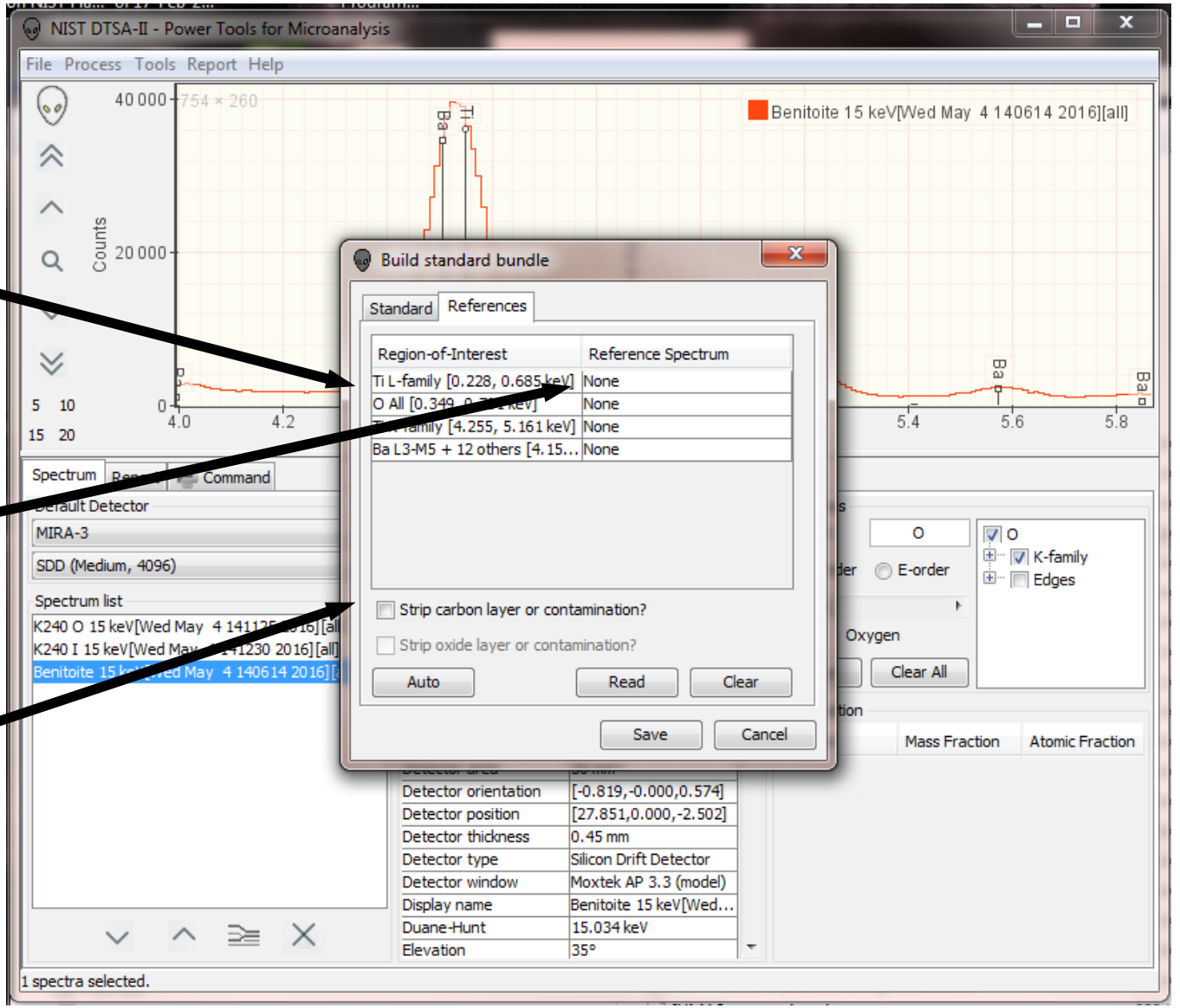


Specifying references

Specifies the references necessary to use this standard.

Specifies the reference spectra for each “region-of-interest.”

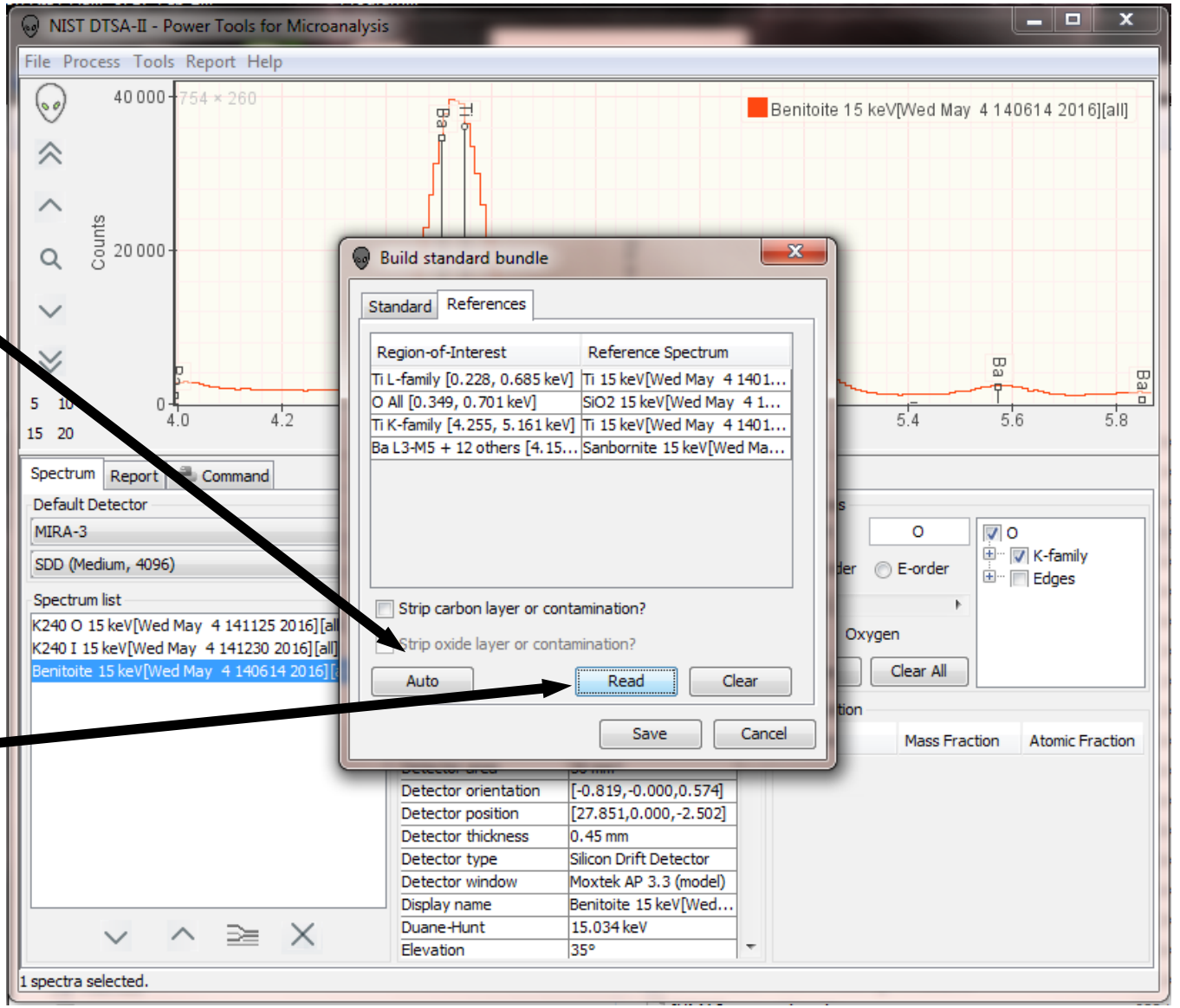
Allows you to also strip spurious C or O if present in the standard spectrum.



Specifying references

Auto-create references by fitting an analytical model to the standard.

Read the references from spectrum files on disk.



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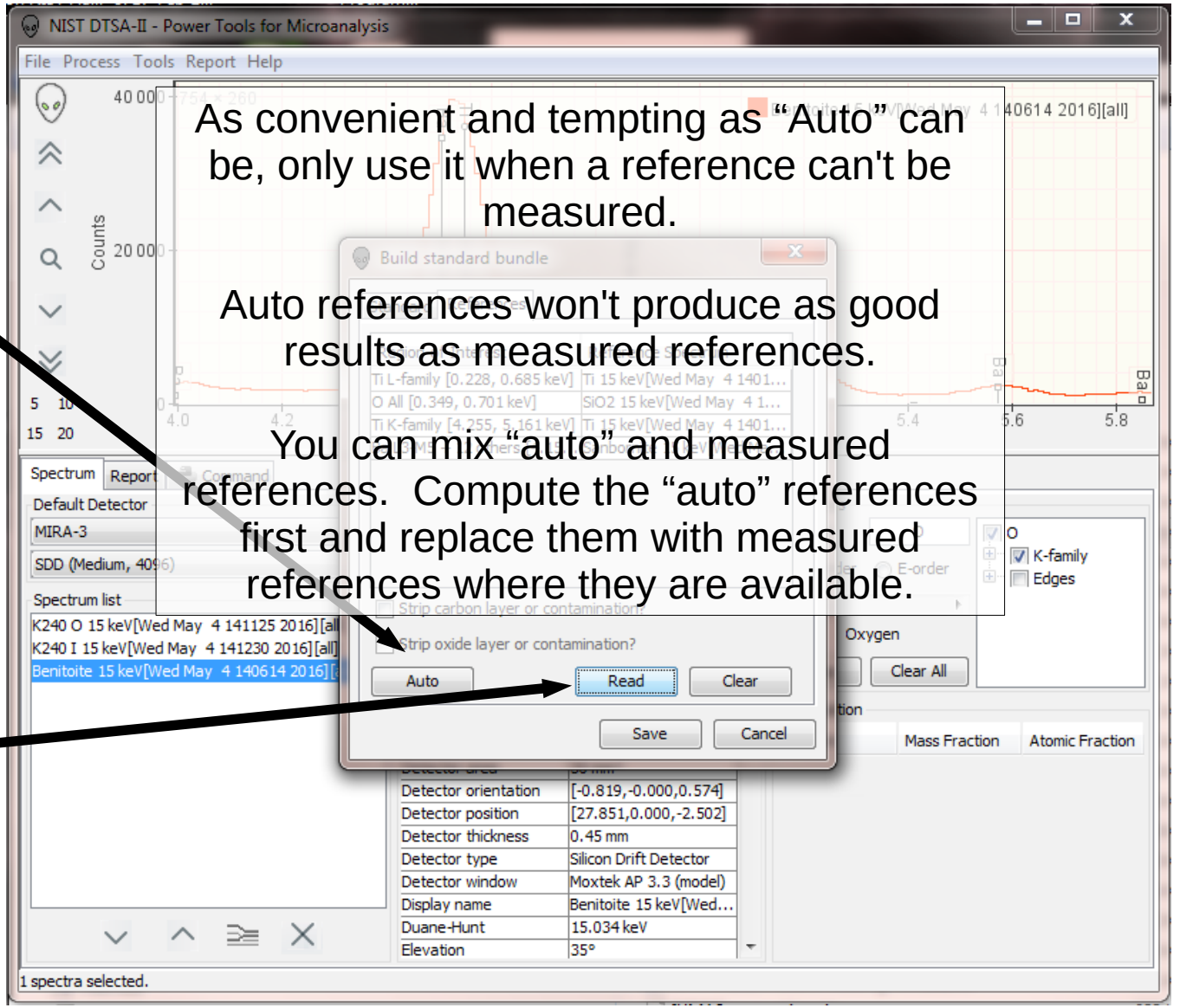


As convenient and tempting as “Auto” can be, only use it when a reference can't be measured.

Auto references won't produce as good results as measured references.

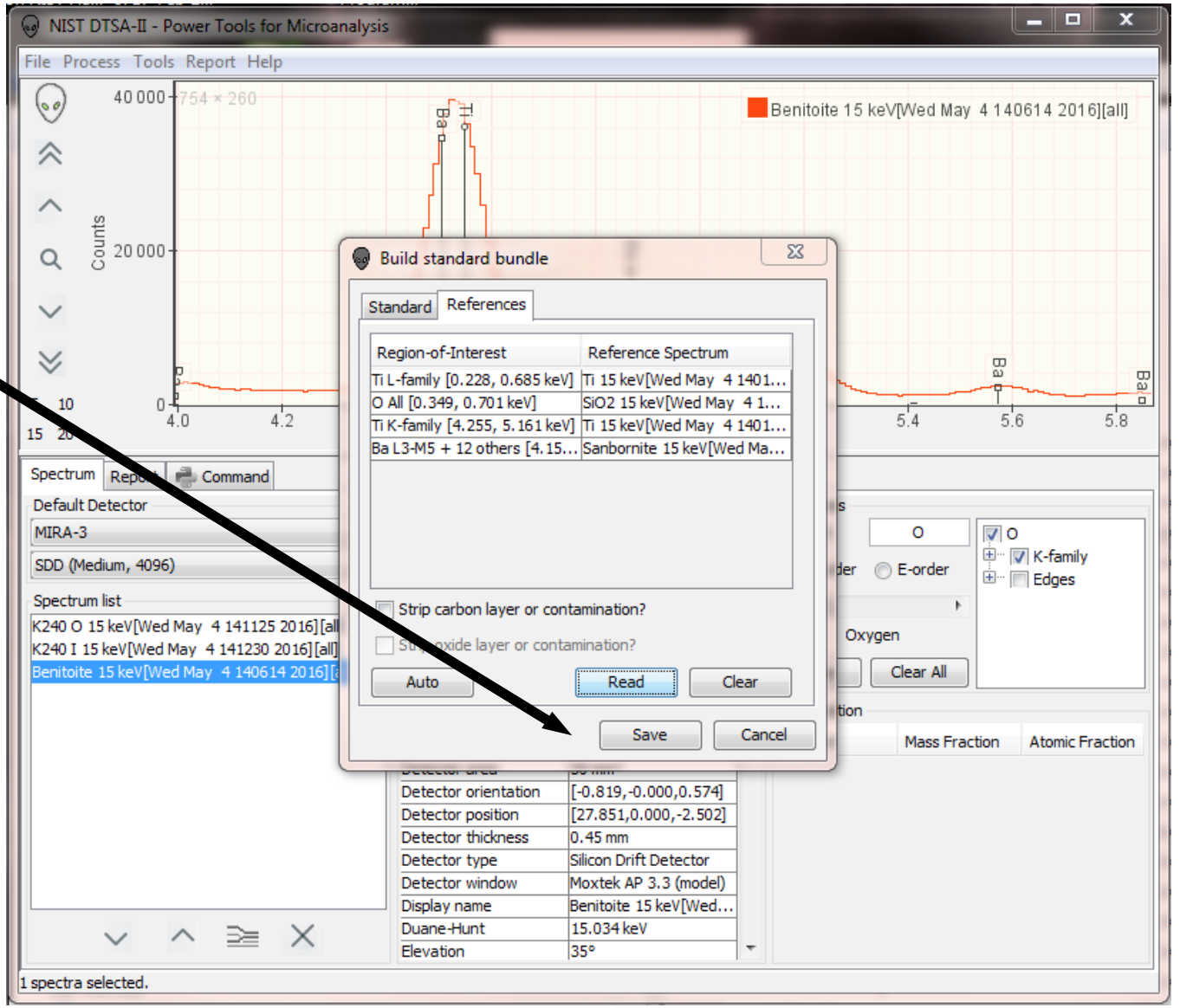
You can mix “auto” and measured references. Compute the “auto” references first and replace them with measured references where they are available.

Saving the standard bundles

When you are done, save the standard bundles to disk.

You will save one bundle of each element for which the spectrum is a standard.

By default, the bundles are named by element and material.



To reiterate

- Standard bundles are designed to simplify using the “Quantification Alien”
- Standard bundles contain:
  - A standard spectrum
  - Zero or more references spectra necessary to use the standard
- References may be missing from the bundle
  - In this case, you will be asked to provide the missing reference when you use the standard bundle in the “Quantification Alien”
- Standard bundles are so convenient that it is generally easiest (but not strictly necessary) if all standard spectra (simple or complex) are transformed into standard bundles.